Standardization of the Inch

THE FACT that the inch is not yet a uniquely defined unit of length presents an important problem to the more advanced inch-using metrologists. These are at least two inches in use in the United States, and three among the inch-using nations of the world. Obviously the differences between these inches are substantially less than when the inch was the breadth of a man's thumb. The fact that the present differences are less than a hundred-thousandth part of an inch has led many to believe that they are unimportant and can, therefore, be ignored. Until fairly recently this was probably true since the most precise measurements of the world's scientists have usually been made in metric units, where there is international accord on a single standard. Advances, however, in modern industrial technology, where the inch is deeply entrenched as the primary unit of measurement, have now reached a stage where efficient interchangeability is impaired by uncertainties in master laboratory standards of as much as a millionth of an inch per inch. And this tolerance is less than the differences between the inches now in use in various countries.

For many years the Bureau has calibrated and certified the best master gage blocks to accuracies within one-millionth of an inch per inch. This tolerance represented a practical limit of combined uncertainties in the measurement technique and in the stability of the gage-block materials. Reference standards of such accuracy were quite adequate for controlling tolerances in production to a ten-thousandth part of an inch, but for controlling production tolerances expressed in a hundred-thousandth part of an inch, they were inadequate.

Several years ago, a group of metrologists from the machine-tool industry urged a program to develop superior gage blocks and associated measurement techniques so that gage-block dimensions could be reliably certified to one or two ten-millionths of an inch per inch. As an indication of their interest, they raised private funds to help finance such a program and at the same time informed members of the Congress of the importance of such work so that for the past 2 years a portion of the Bureau's appropriation has been specifically earmarked to meet this objective.

National standard of length, Prototype Meter Bar No. 27. The distance between two parallel lines engraved on this platinum-iridium bar defines the meter for all length measurements made in this country.

Although there are many technical problems which have to be solved to achieve standards of such accuracy, progress has been reasonably good. The first problem concerns the international meter from which our own "English" length standards are derived. The international meter is known with an accuracy of about one part in ten million, which is not quite precise enough to permit accurate subdivision and transfer to end standards whose lengths must be known to a ten-millionth part of an inch per inch. Under the guidance of the International Committee of Weights and Measures, work is in progress in all the major national standardizing laboratories throughout the world toward an atomic standard for length measurement. It is expected that by 1960, international accord will be reached on using the wavelength corresponding to a specific energy transition in a specific type of atom as the ultimate standard for all length measurements. As a result of the most recent conference of the experts on this subject, it appears that the most favored standard is an orange line of the element krypton 86. Most of the essential activities required for the satisfactory solution of this phase of the standards problem are already in process. There is, however, need to consolidate opinion and initiate action to standardize the inch, the unit of measurement which is fundamental to most important industrial dimensional-measurement processes, particularly in the machine-tool industries, in all the English-speaking nations.

The United States, the United Kingdom, and Canada each has a different inch. The differences between these inches are such that a precise reference standard such as an end standard or gage block, calibrated according to the standards of one of these nations, may fail to meet tolerances in the other two. These differences resulted in some confusion and inefficiency during World War II. In view of the continuing need for increased precision in the years ahead, these differences, unless resolved, will become severe obstacles to the future exchange of precision instruments and components.

Background of Present Length Standards

The difficulties under which commerce had been carried out among the Thirteen Colonies presumably were responsible in part for that farsighted provision of the Constitution which delegated to Congress the authority "to fix the standard of weights and measures", but for 80 years no formal action was taken by Congress to "fix" the standards, save for the adoption in 1828 of a standard Troy pound for coinage purposes.

Jefferson, as Secretary of State, presented in 1790 an elaborate report on weights and measures, including the proposal of a standard of length based upon the length of a uniform second's pendulum. In 1795, President Washington presented to the Congress a communication from the Minister of the French Republic suggesting the adoption by the United States of the metric system of weights and measures, which France had adopted 4 years earlier. This proposal, however, met with little favor.

This article presents the substance of an address delivered by Dr. A. V. Astin, Director of the National Bureau of Standards, to the Dimensional Standards & Metrology Division of the American Ordnance Association, Bedford, Mass., on January 16, 1958. The historical material was prepared by Dr. Lyman J. Briggs, Director Emeritus, in support of a legislative proposal in 1938.

Meanwhile, State Legislatures were imploring Congress to take some action to bring about uniformity; and in 1821, John Quincy Adams, as Secretary of State, urged Congress "to fix the standard with the partial uniformity of which it is susceptible at present, excluding all innovations. To consult with foreign nations for the future and ultimate establishment of universal and permanent uniformity."

In 1830 the Treasury Department was instructed through a resolution of the Senate to investigate the weights and measures in use in the various customs houses of the country, with a view to bringing about uniformity in the collection of customs. The Secretary of the Treasury gave a broad interpretation to this authority to "investigate" and the outcome was the adoption by the Treasury Department, without further action by Congress, of an avoirdupois pound of 7,000 grains, a yard of 36 in., a wine gallon of 231 in.^{3}, and a Winchester bushel of 2,150.42 in.^{3}, for use in the collection of customs.

So well pleased was Congress with this solution that the Secretary of the Treasury in 1836 was directed to deliver to the governor of each State a complete set of all the weights and measures adopted as standard by the Treasury Department. Although no Congressional

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action was taken to legalize these standards, many of the States adopted them independently, and a groundwork for uniform weights and measures was at last provided.

It was not until after the Civil War that Congress took the first formal steps to legalize a system of weights and measures, and this, oddly enough, did not refer to the weights and measures in common use, but to the metric system, rejected in 1795.

We thus have the anomalous situation in this country of a legalized system of metric weights and measures which is not in common use, and a customary system of weights and measures which has never been formally legalized. However, in the Act of 1866, Congress did include a table of conversion factors which "may lawfully be used" in going from one system to the other. That Congress intended this table only as an approximation to the true ratio of the units in the two systems is evident from the fact that the meter is given as equivalent to 39.37 in., while the millimeter is rounded off as equal to 0.0394 in.

The platinum-iridium meter and kilogram, supplied to our Government as a result of its participation in the Metric Convention of 1875 and made available in 1890, provided this country with far better material standards than it had ever had before. Both the meter bar and the kilogram had been carefully compared with the in-ternational prototypes, and the coefficient of expansion of the meter bar had been measured. They constituted, together with the troy pound, the only legal material standards possessed by the Government. Accordingly, in the absence of further Congressional action, Superintendent Mendenhall of the Coast and Geodetic Survey in 1893 issued the following order: "The Office of Weights and Measures with the approval of the Secretary of the Treasury, will in the future regard the international prototype meter and kilogram as fundamental standards, and the customary units, the yard and the pound, will be derived therefrom in accordance with the act of July 28, 1866." To pass from the meter to the inch, the Office of Weights and Measures adopted the conversion factor, 1 m equals 39.37 in. exactly, as set up in the Act of 1866; and this ratio has been adhered to in the length calibrations of the Bureau and in the surveys and maps of the Coast and Geodetic Survey. This ratio gives an inch approximately equal to 2.540005 cm.

The rapid growth of science and technological industry near the end of the 19th Century led to increased interest in units and standards for physical measurement. This interest led to the establishment of the Bureau in 1901, and to efforts to extend the use of the metric system. A bill was introduced in Congress in 1902 to make the metric system mandatory. The bill had extensive popular and Congressional support but the sponsors finally withdrew the bill in the face of growing opposition from some groups. Support for compulsory use of the metric system has gradually declined since that time but there are still sporadic attempts to require the use of the metric units of measurement.

Nevertheless, metric measures continued to find increased application on a voluntary basis, particularly as their use increased in the non-English speaking nations. By the early 1930's metric measures were of sufficient importance in American industry to bring pressure for a simple factor for converting inch measures to metric measures. These pressures led the American Standards Association to approve in 1933 an American Standard for Inch-Millimeter Conversion for Industrial Use, in which the inch was defined as 25.4 mm. This relatively simple conversion factor permitted, for example, the use of 127 or 254 toothed gears for the direct conversion on many machine tools of inch measures to metric measures.

In recognition of the growing importance of the 2.54-cm inch to American industry, in 1938 the Bureau sponsored legislation in the Congress to define this ratio as the standard for the English dimensional measures. However, strong opposition to the proposed law developed among the Nation's civil engineers and map makers and the Coast and Geodetic Survey. As previously mentioned, in the days when this agency had responsibility for the weights and measures standards, its superintendent, T. E. Mendenhall, proclaimed the meter as 39.37 in., yielding an inch approximately 2.540005 cm long. The basis of the Coast and Geodetic Survey's opposition stems from a

A wavelength of light from the krypton 86 lamp has been proposed for international adoption as the primary standard of length. The lamp, housed in aluminum container (center of photo), is operated at solid nitrogen temperature.

Representatives from industry view demonstrations of interferometer for measuring deviations from parallelism of end surfaces of precision gage blocks. This instrument was developed as part of a program to make possible the regular calibration of gage blocks by the Bureau to an accuracy of 1 part in 10 million. *Left to right:* M. C. Curtis, The Timken Roller Bearing Co.; J. K. Emery, The Van Keuren Co.; Dr. E. S. Rowland, The Timken Roller Bearing Co.; R. T. Mcrae, The DoAll Co.; I. H. Fullmer, National Bureau of Standards; R. V. Ellstrom, Dearborn Gage Co.; A. B. Richards, Ford Motor Co.; and J. B. Saunders, National Bureau of Standards.

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very real problem which still would exist if their standard of measurement were changed.

The Coast and Geodetic Survey has established plane coordinate map systems for each of the 48 states. The coordinates of some 150,000 triangulation and transverse points have been established and the values published in both feet and meters. These are in turn used by surveyors and engineers in fixing boundaries throughout the Nation. Changing the inch to equal 2.54 cm exactly would result in changing the proper values for thousands of these reference points by as much as 3 or 4 ft. It should be noted that the locations of these points from the origins of their respective coordinate systems are not known to this accuracy; nonetheless, the coordinates of the various reference points are expressed to the nearest foot, and various other positions and boundaries are established in terms of distances from the coordinate reference points. In addition, these boundaries in terms of the foot values of the coordinate points have legal status by virtue of legislative action in many of the States.

It has been thought by some that since the difference between the two inches under discussion (about 2 parts in a million) is about 10 times smaller than the uncertainties in the surveys, a change from one inch to the other should make no real difference to the map makers. But since the coordinate values of most of the points have been defined more precisely than their true positions are known, the problem of a change in the inch is a very real one. The metric coordinate values of the surveys, which are published along with the foot values, would of course be unaffected by the change. As a result of opposition based on the problem just discussed, the 1938 bill failed to be enacted into law.

Again between 1945 and 1947, efforts were made to secure legislation defining the inch as 2.54 cm. The renewed effort, which had the support of the Army and Navy, grew primarily from difficulties encountered in World War II in attempting to interchange various precision products between Great Britain and the United States. The American Standards Association conducted an extensive industry survey in an effort to build up support for such legislation. The same opposition again stopped any legislative action.

In 1952, the National Advisory Committee for Aeronautics, acting on a recommendation of the International Civil Aviation Organization, adopted the 2.54-cm inch for use in altimetry and airspeed computations, and in defining the standard atmosphere.

Interest in the problem was stimulated again at the Bureau in 1954 as a result of discussions with representatives of other inch-using nations in the hope of achieving some sort of international standardization of this important but multivalued unit.

Situation in the United Kingdom

The British length standard is the Imperial Standard Yard, a bronze bar, established by Act of Parliament in 1878 as the national standard. This particular standard had been constructed as replacement for an earlier standard which was destroyed by fire in 1834. The British also have a copy of the international meter and comparisons between the two are occasionally carried out. The comparisons have yielded the following values for the British inch: In 1895, 25.399978 mm; in 1922, 25.399956 mm; in 1932, 25.399950 mm; and in 1947, 25.399931 mm.

The change in the ratio of the metric to English standards is generally attributed to a shrinking of the Imperial Yard, since all evidence points to the platinum-iridium meter bar as the more stable object. The British National Physical Laboratory has arbitrarily selected the 1922 ratio for use in calibrating the most precise measuring devices. An inch standard based on this ratio is about two parts in a million shorter than the ASA inch and four parts in a million shorter than the inch used in calibrations by the Bureau.

In 1951 a British Committee on Weights and Measures Legislation recommended the abandonment of the Imperial standards and the gradual replacement in ordinary use of English measures by metric measures. It recommended that the yard be defined as equal to 91.44 cm exactly, which gives a 2.54-cm inch. They further recommended that efforts be made to bring the British and United States measures into as close agreement as possible.

Situation in Canada

The Canadian Parliament in 1951 established the yard as the unit of length but based its value upon the international meter. The legal ratio defines the yard as 0.9144 m, again equivalent to the 2.54-cm inch.

Situation in Australia

The Australian Parliament in 1948 passed a Weights and Measures Act which provided for a National Standards Commission to establish standards for various units of measurement. The Commission has not formally proclaimed a value for the yard or inch, but information based upon informal discussion with some members of the Commission indicates preference for the 2.54-cm inch.

Proposal

Efforts should be initiated to establish an international yard through negotiations with representatives of appropriate standardizing agencies of the major English-speaking nations. The international yard would be based on the international meter and defined as 0.9144 m exactly. This, of course, would yield an international inch equal to 2.54 cm.[1] The yard is suggested as the primary length unit for standardization because of its traditional position as the primary English dimensional standard. The initial mechanism for achieving such a standard might be through agreements between the various national standardizing laboratories.

There is precedent for such an approach. Agreement was reached in 1954 on an International Nautical Mile through a somewhat similar technique. The mechanism used to achieve agreement in 1948 on the American-British-Canadian screw-thread standard provides another related precedent.

This approach would not require legislation by the Congress although ultimately it might be desirable. The Coast and Geodetic Survey could continue the use of their present units as long as it appears necessary or desirable. These units might be referred to as Mendenhall units in recognition of the individual primarily responsible for their present status. Should agreements on international English units be reached, the Bureau would then certify appropriate length calibrations in terms of the international units unless a specific request was made for values in terms of the older units.

[1] *This value is exactly the Canadian standard, 2 parts per million smaller than the United States standard, and about 2 parts per million larger than the British standard.*

Interaction of Direct Azo Dyes in Aqueous Solution

BUREAU research on the properties of materials is providing evidence of a fundamental relationship between the attachment of direct azo dyes to cotton and the chemical association of these dyes in mixtures.[1] The correlation results from a current study of spectral changes of organic dyes as caused by light, heat, and concentration variables. Partially sponsored by the Air Force Office of Scientific Research, the program is being conducted by J. H. Gould and M. N. Inscoe in collaboration with W. R. Brode, Associate Director of the Bureau. While the results apply primarily to changes in solution, they may provide a valuable basis for further investigations of dye adherence to fabrics.

Direct, or substantive, azo dyes have a strong affinity for cellulose and adhere directly to the fibers when applied from a boiling neutral solution. This is important in the textile industry since cotton is 99-percent cellulose and since the structure of rayon is also based on this fundamental molecule.

The behavior of direct dyes applied from dye baths containing mixtures of dyes often differs from that of the individual dyes. In general, the altered characteristics are attributed to interaction or complex formation between unlike molecules and include an increase in time to reach equilibrium, a decrease in the amount of one or both of the dyes absorbed at equilibrium, or a greater unevenness in the dyeing.

When the absorption spectrum of a mixture of azo dyes in aqueous solution is not the same as the sum of the spectra of the individual components in separate solutions, the result is called a "nonadditive" spectrum. Because the absorption curve is an inherent character-

The absorption spectra of a mixture of two dyes is often the same as the sum of the two individual components' spectra, (left) metanilic acid and sulfonic acid blue B. Two unlike direct dyes interacting in solution produce a nonadditive spectrum, (right) benzo blue and brilliant yellow dyes.
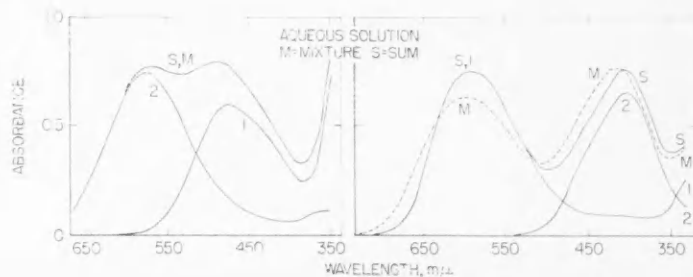
Molecular models of representative direct dye, congo red, and an acid dye, amaranth.

istic of the dye molecule, nonadditive spectra are indications of interaction. No spectral changes were noted when aggregation occurred at the concentrations used in this study. Aggregation is defined here as the complex association of like molecules.

In the present experiments, 30 direct azo dyes differing in aromatic components, number of azo groups, and arrangement of substituents were studied in various combinations. To insure solubility in a water solution, all of these dyes were sulfonic acid ($-SO_3Na$) derivatives.

To obtain the graphic addition spectrum of two individual dyes, the two dyes in separate solutions were measured simultaneously in the spectrophotometer. Then, the same components were mixed and remeasured. If this latter spectrum was not the same as the initial spectrum, it was assumed that interaction had taken place.

Although mixtures of direct dyes usually gave nonadditive spectra, there were two general situations in which additive spectra were obtained instead of the expected nonadditive curves. In the first of these, the steric hindrance by central sulfonic acid groups prevented interaction between the two dyes. This effect is caused either by the bulkiness of the acid groups, which could interfere with the close approach of the molecules of the dyes, or by the mutual repulsion between the like negative charges, which could also hinder the molecules from drawing near each other. Additive spectra were also noted when the terminal groupings on both components were identical or very similar. It is probable that interaction may occur in such cases but does not produce marked spectral changes because of the similarity between the two dyes. Interaction in such a mixture is comparable to aggregation in a solution of the individual dye, and the degree of aggregation does not produce significant mole behavior with direct azo dyes.

The acid azo dyes, as opposed to the direct azo dyes, neither adhere directly to cotton nor are they appreci-ably aggregated at higher concentrations or by inorganic salts. An acid dye generally contains a shorter conjugated chain (alternating double and single bonds) than does a direct dye. The repulsion of the negatively charged sulfonic acid groups on the molecule and the increased solubility caused by these groups are effective in keeping the molecules separated. Because of these factors, the dyes show little tendency toward interaction in mixtures with the direct azo dyes.

Basic dyes, e. g., methyl violet or methylene blue, as well as some substantive fluorescent brightening agents, were shown to give nonadditive spectra in mixtures with various other dyes.

The presence of foreign substances in the dye solution influences the state of aggregation of the dyes as well as their behavior in dyeing. The addition of inorganic salts increases aggregation of the dye as well as the amount of dye taken up by the fiber. Other substances may have an opposite effect. For example, pyridine inhibits the aggregation of azo dyes and also decreases the affinity of these dyes for cellulose to such an extent that it can be used as a "stripping" agent to remove the dye from the fiber. Such substances also influence the interaction of azo dyes in mixtures.

Alcohol and nonionic detergents—both effective in decreasing the aggregation of direct azo dyes—prevent interaction. Mixtures of dyes that normally give nonadditive spectra gave additive spectra in solutions containing 40-percent alcohol or 0.1 percent of a nonionic detergent. On the other hand, the addition of inorganic salts or a large increase in the dye concentration produced spectral changes which indicated greater association between the dyes.

[1] *For further technical information, see* The relation between the absorption spectra and the chemical constitution of dyes: XXIX. The interaction of direct azo dyes in aqueous solution, M. N. Inscoe, J. H. Gould, M. E. Corning, and W. R. Brode, J. Research NBS **60**, 65 (1958) RP2823.

Retardation of Copper Corrosion by Light

SUNLIGHT or other intense light, which ordinarily accelerates the corrosion process in metals, has been found to produce an opposite effect on copper-oxidation [1]—copper-oxide growth is actually retarded by the irradiation. This unusual behavior was observed at the Bureau as part of a continuing research project on the corrosion of copper over a wide range of controlled conditions.

In the present investigation, which was partially sponsored by the Corrosion Research Council, Jerome Kruger of the corrosion laboratory immersed copper single crystals in water and found that irradiation retarded subsequent copper-oxide growth. Single copper crystals were used because their relatively simple structure gives results that are more easily calculated and understood.

The copper crystals, which were grown from copper of 99.99-percent purity, were submerged in air-saturated, distilled water. A water-jacketed container was used to maintain a constant temperature and to avoid overheating due to intense light. All light was excluded from the highly polished copper crystal except that which shone through a small aperture in the jacket.

After 3 hours of uniform illumination at room temperature by a 3,200° K tungsten lamp, the entire crystal sphere was found to be much less oxidized than when illuminated by room light. To study this effect further, one-half of the crystal was illuminated with the intense white light from the tungsten lamp. It was found that
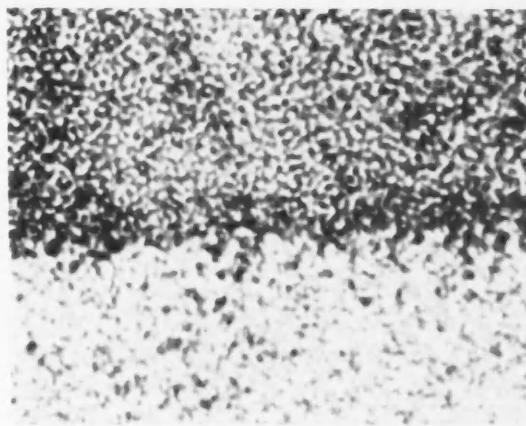
Micrograph (magnified 400 times) illustrating well-defined boundary between unexposed (upper region) and illuminated areas of partly-oxidized crystal surface.

Micrograph showing copper single crystal, oxidized in air-saturated distilled water. Upper portion, kept dark, became corroded, while lower surface—exposed to light from a 3,200° K tungsten lamp—was much less oxidized. Stem protruding from bottom permits crystal to be held stationary.

the irradiated portion had oxidized at a markedly different rate than the unilluminated area. An electrometric-measuring technique showed a film thickness of 120 A on the exposed side, and an average film thickness of 500 A on the other side.

When similar light was allowed to impinge on part of a crystal already coated with a thick film (1000 to 2000 A), the oxide on the illuminated portion became considerably thinner than on the unexposed part of the crystal. X-ray diffraction studies of the films found on both the dark and the irradiated parts of the crystal showed that the films were composed of well-oriented cuprous oxide.

Although the mechanism for this behavior is not known, a possible explanation is a copper-cuprous oxide photocell theory, which centers upon the semiconductance of cuprous oxide. Irradiation would cause an electron flow from the cation-deficient semiconductor film of Cu_2O into the metal. This direction of flow is just opposite to that during oxide growth and hence would block further propagation of the oxide. Other investigators [2,3] have found that light favors oxidation of aluminum and tantalum whose oxides are cation-excess semiconductors.

The present study indicates that there is direct correlation between the rate of the oxide formation in water and the underlying crystal structures. Crystallographic orientation studies are now in progress to verify this.

[1] Inquiries concerning further information on copper corrosion should be addressed to Dr. Jerome Kruger, Corrosion Metallurgy Laboratory, National Bureau of Standards, Washington 25, D. C.

[2] N. Cabrera et al., Compt. rend. acad. sci. (Paris) **224**, 1558 (1947).

[3] D. A. Vermilyea, J. Appl. Phys. **26**, 489 (1955).

TELESCOPIC OBSERVATIONS strongly suggest that Mars has an atmosphere similar to, though more transparent than, the atmosphere of the Earth. For more specific information on the Martian atmosphere, astronomers have relied mainly on the spectroscope or spectrograph, instruments that analyze the sunlight reflected from the planet's surface. In principle, the gases present should reveal themselves by their characteristic absorption lines and bands, but results so far have not been conclusive. However, the persistence of inconclusive results, despite increasing sensitivity of observing techniques, has led to lower estimates of the quantities of gases, such as oxygen, water vapor, and carbon dioxide, that may be present on Mars.

Another attack on this problem has been made by scientists of the Bureau, and they have now completed analysis of the spectrograms obtained during the close approach of Mars in the late summer of 1956.[1] Two husband and wife teams—C. C. Kiess, H. K. Kiess, C. H. Corliss, and E. L. R. Corliss—participated in the investigation which was sponsored jointly by the National Geographic Society and the Bureau.

Using more sensitive instruments than have previously been applied to this purpose, the scientists photographed the Martian spectrum under the excellent observing conditions at the new high-altitude observatory, operated by the United States Weather Bureau, on Mauna Loa volcano in Hawaii. Also, in an effort to extend observations farther into the infrared, another set of spectograms was made at the Georgetown College Observatory in Washington, D. C.

The investigation concentrated mainly on a search for oxygen and water vapor. The results indicate that both of these, if present, occur in quantities too small to be detected with the equipment used. On the basis of laboratory tests of spectrograph sensitivity to water vapor, this means that there is less H_2O in the Martian atmosphere than there is in a film of water 0.08-mm (1/300-in.) thick. The spectrograms also showed no trace of the carbon dioxide lines that have been observed in Venus, or of spectral lines of the noble gases.

It is believed that these results are not incompatible with the presence of water vapor in amounts sufficient to explain, for example, the transport of water from one polar cap to the other. It is now fairly well established that the white polar caps of Mars consist of solidified H_2O, and it is reasonable to suppose that the seasonal process in which one cap shrinks while the other expands is due to the transfer of water vapor over the Martian surface.

The results do raise the question, however, as to whether the spectroscopic tests hitherto used are delicate enough for the purpose. In the case of H_2O molecules, there is reason to believe that the bands that have been used (because of accessibility to present methods of observing) are not the most sensitive ones. Both theory and experiment indicate that much stronger bands occur farther in the infrared, but different or improved techniques are needed to detect them on Mars. The use of spectrographs mounted in high-altitude balloons, rockets, or artificial satellites will reduce the difficulty further.

Methods

The light from Mars, as received near the Earth's surface, is really a composite of three different spectra. Specifically, it contains absorption lines originating in: (1) The reversing layer of the Sun's atmosphere, (2) the atmosphere of Mars, and (3) the atmosphere of the Earth. The wavelengths of the solar lines are accurately known and so can easily be identified. For the much more difficult task of distinguishing lines due to Mars from those due to the Earth, two methods have been in use.

One method is to observe Mars at "opposition", that is, when Mars, Earth, and Sun are most nearly in a straight line, with the Earth between the other two. Its distance from the Earth being a minimum (or nearly so), Mars is then at its brightest. Also, because the distance between Mars and the Earth is neither increasing nor decreasing, absorption lines originating in the atmosphere of Mars will not be separated by Doppler
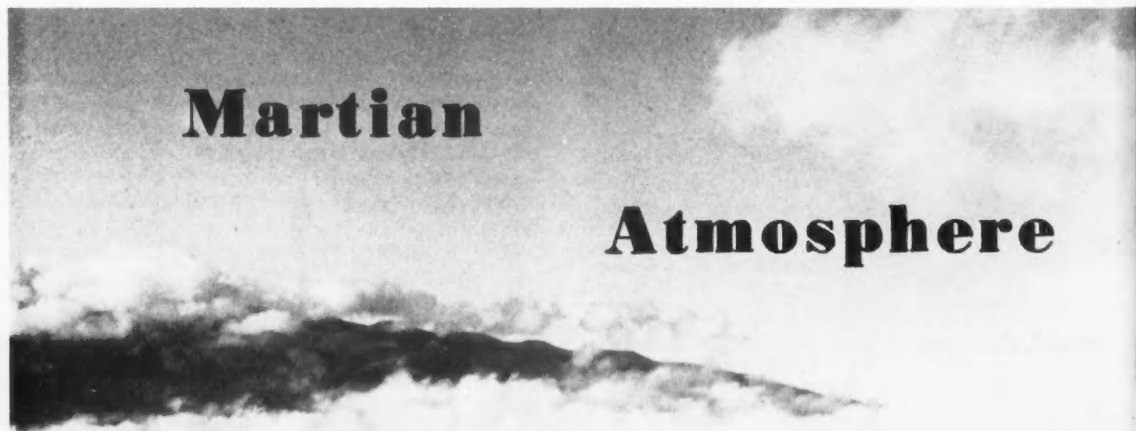
Martian
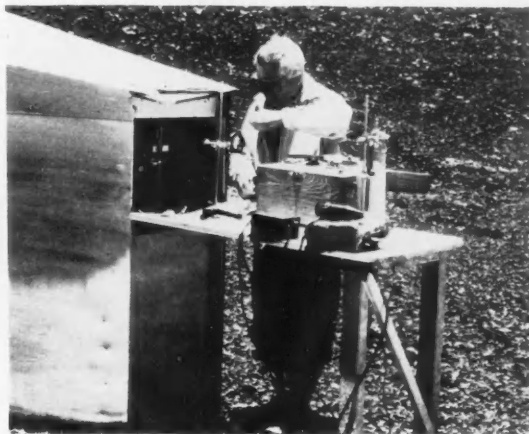
Atmosphere

shift from those originating in the Earth's atmosphere; so that oxygen lines, for example, from Mars will be superimposed on those from the Earth. In such a case, the line may be noticeably intensified or, more likely, distorted; that is, since the Doppler shift is not negligibly small except for a brief interval, the intensity profile of such a line, as measured with a microphotometer, would be asymmetrical. Such distortions might be detected more readily by comparison with corresponding lines in the spectrum of the Moon (which has no atmosphere of its own).

The second method is to observe Mars at some time before or after opposition, when the Doppler shift would separate clearly the Martian from the terrestrial lines. Then, if there is oxygen in the atmosphere of Mars, one might expect the oxygen lines caused by the Earth's atmosphere to have faint companions separated by the amount of the Doppler shift.

Comparison with the spectrum of the Moon, obtained under similar conditions, would allow the Doppler shift to be measured—for example, by the relative displacement of the solar lines. Comparing the Martian spectrum with the more familiar spectrum of the Moon

would also help in detecting any unknown lines that might show up.

The second method was used in the present investigation. Spectrograms were obtained about 7 weeks before opposition at Mauna Loa and about 6 weeks after opposition at the Georgetown observatory. In the earlier spectograms, the Doppler shift was 0.22 A (angstroms) towards the short wavelengths, and in the later ones 0.25 A towards the longer wavelengths. The measured values of the shift agreed well with the values calculated from the orbital velocities of Mars and the Earth.

Instruments

The new study of the Martian spectrum was undertaken in order to see what could be done with the newer aids to observation. These include better diffraction gratings and optical systems, faster photographic plates, and more accurate guiding mechanisms for prolonged photographic exposures.

Before proceeding to Hawaii, the scientists tested the feasibility of using high-dispersion concave gratings for planetary spectroscopy at the Georgetown observatory. Various arrangements were tried out on Jupiter, which was then about as bright as Mars would be in July 1956. The tests justified proceeding with the project and showed that the mounting devised by Wadsworth would be suitable for the grating.

Light is gathered from Mars with a siderostat, a mirror that is motor-driven (with manual fine adjustment) so that the light is always reflected in the same horizontal direction towards the rigidly mounted telescope lens and spectrograph. The telescope lens focuses an image of the planet onto a slit, and the light passing through is converted into a parallel beam by a collimating mirror. The beam then strikes and is reflected from a concave diffraction grating which

Restudied

spreads the light out into its components according to wavelength. The light as thus spread out—i. e., the spectrum—falls upon a thin glass photographic plate which is curved to fit the focal plane of the grating.

Two diffraction gratings were selected. One was ruled by R. W. Wood at Johns Hopkins University and has 15,000 lines per in. and a (reciprocal) dispersion of 5 A per mm. The other, ruled by H. G. Gale at the University of Chicago, has 30,000 lines per in. and a dispersion of 2 A per mm. Both have the special virtue of concentrating much of the light in one of the first-order spectra. The telescope lens, 12 in. in diameter and 12 ft in focal length, was made by J. Clacey, former chief optician at the Bureau.

Observations

The observatory on Mauna Loa offers many advantages to the astronomer. Situated in the midst of the Pacific at an altitude of 11,134 ft, it is free from the ruggedness of terrain that produces turbulence in the surrounding air. Particularly important is its height of about 1 mile above the inversion layer of the atmosphere. This is the level at which the temperature of the air starts to increase with increasing altitude; the bulk of atmospheric dust and moisture are trapped below it.

Built for the joint use of the United States Weather Bureau and the National Bureau of Standards, the Mauna Loa observatory was only recently put into service.[2] In fact, the scientists making the present study arrived in time for the dedication ceremonies and began the Mars observations immediately afterwards.

Spectra of Mars and the Moon were obtained successively on the same plate, the exposures to Mars lasting 3 hr each. The Wood grating was tried first. The spectrograms proved sufficiently dense to warrant using the more dispersive Gale grating, which was then set up to photograph wavelengths from 5800 to 7400 A.

The Doppler shift is clearly evident in the best spectrograms. In several cases, lines of solar origin that are hidden behind terrestrial lines in spectrograms of direct sunlight are shifted out of their hiding places and appear separately in the spectrum of Mars. If any lines, due to water vapor or oxygen in the atmosphere of Mars, appeared in the spectrum, they should be shifted by about 0.22 A from those of terrestrial origin. However, there are no companion lines to be seen with the strong lines either in the Fraunhofer B band of O_2 (roughly

Spectra of Mars (a) and Moon (b) obtained on Mauna Loa, July 1956. Distance of Mars was decreasing so there is a Doppler shift (arrows) in the Martian spectrum towards shorter wavelengths. This only affects lines originating on Mars or present in the original sunlight that Mars reflects. At the strong absorption line, 7187.38 A, a blend of a solar iron line and a terrestrial water-vapor line, the shift is sufficient for the iron line to form a new blend with the H$_2$O line at 7187.01 A.
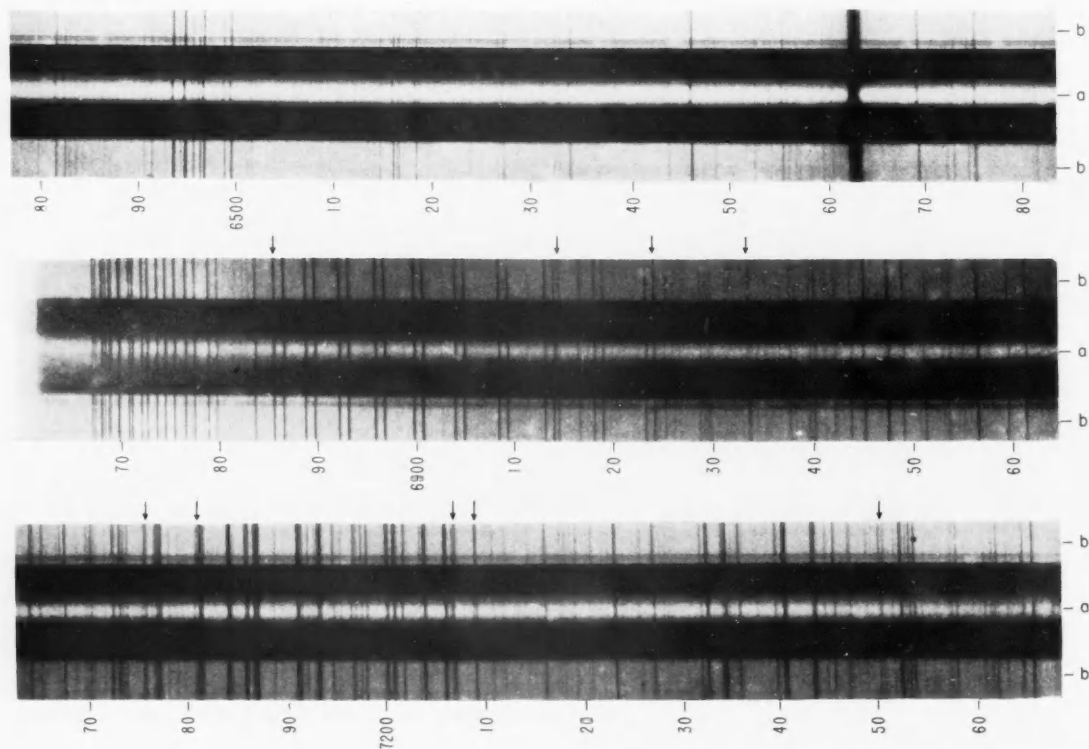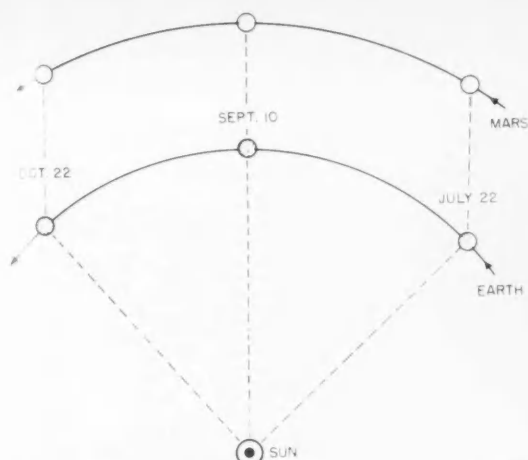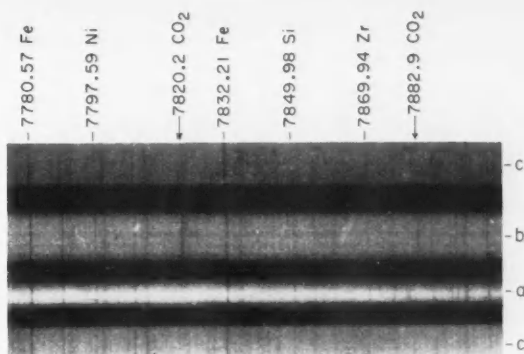
Approximate relative positions of Mars, Earth, and Sun in 1956 when spectrographic study of Martian atmosphere was made. On September 10, when Mars was "in opposition", its distance from the Earth was a minimum. Spectrograms were obtained around July 22 and again around October 22 when this distance was decreasing and increasing, respectively.


High-dispersion spectra of Mars (a), Venus (b), and the Moon (c). The carbon dioxide lines at 7820.2 and 7882.9 A appear in the spectrum of Venus, but not in that of Mars (nor of the Moon).

6870 to 6940 A) or in the *a* band of H_2O (roughly 7200 to 7300 A).

Later, the spectrograph was set up again at the Georgetown College Observatory. The aim was to extend observation farther into the infrared than was possible at the time on Mauna Loa. The lower altitude of Washington, D. C., made it necessary to use the Wood grating; exposures to Mars were each about 5-hr long. The portion of the spectrum from 5000 to 9000 A was photographed and scanned for lines of atomic nitrogen, oxygen, and the noble gases, as well as for the *A* band of O_2 (about 7600 to 7700 A), the H_2O band at 8200 A, and the CO_2 bands at 7820 and 7889 A that were found (1932) by W. S. Adams and T. Dunham, Jr., in the spectrum of Venus. Again the Doppler shift was clearly evident, but none of the lines sought for could be detected.

Interpretation

The results of this investigation, which extended over a greater wavelength range and utilized higher dispersion than those previously reported, confirm the findings of W. S. Adams and T. Dunham, Jr.[3] in 1934 and 1941, with respect to the low abundance of oxygen and water vapor in the atmosphere of Mars. The numbers of molecules of both gases are too small to be detected with the equipment used.

In the case of water vapor, tests with a spectrograph of dimensions close to those of the one used in this study were made in the Bureau's spectroscopy laboratory. Under conditions in which the water vapor in the light path was equivalent to a water film 0.15-mm thick, a few of the strongest lines of the *a* band and the one at 8200 A were detectable. Since none of these were detected in the spectrum of Mars, the water-vapor content of its atmosphere must be less than that of a film of water 0.08 mm, or half of 0.15-mm thick; this is because the light from Mars passes twice through its atmosphere—once coming from the sun and once after reflection from the Martian surface.

The spectrograph used in the present investigation could detect no H_2O bands beyond the one at 0.823 μ (1 μ = 10000 A). However, theoretical analyses by E. K. Plyler and W. S. Benedict [4] of the Bureau's radiometry laboratory, and others, indicate that the bands at 0.942, 1.135, and 1.379 μ are more intense. As shown in table 1, the band at 0.942 μ is about 3 times, the one at 1.135 μ about 10 times, and the one at 1.379 μ at least 60 times more sensitive than the band at 0.823 μ. C. C. Kiess was able to detect the bands at 0.942 and 1.135 μ in the laboratory, where a strong source of artificial light was available.[5]

Nonetheless, if water vapor is to be detected in the relatively weak light from Mars by means of the longer-
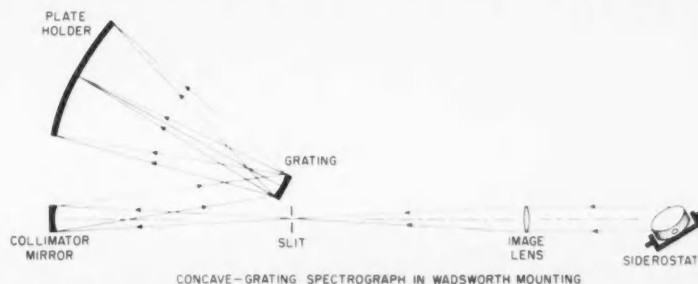
Equipment setup used in spectrographic study of Martian atmosphere. Siderostat mirror is electrically rotated to compensate for the Earth's daily rotation, so that the light from Mars is reflected in a fixed horizontal direction towards the telescope image lens and the concave-grating spectrograph.
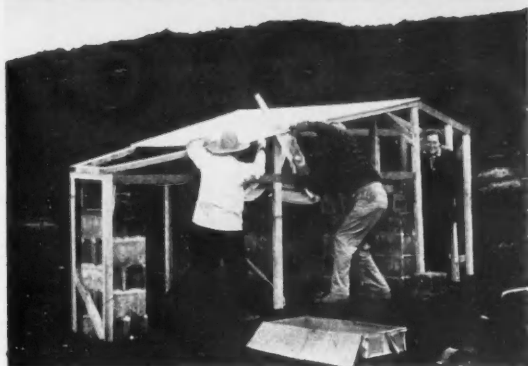
Left: **Erecting the shelter for the spectrograph.** *Below:* Table in front of opening in spectrograph shelter, showing equipment used to guide the siderostat mirror (not visible). Observer looks through round magnifying glass (left) at image of Mars on spectrograph slit. When image tends to deviate from slit, observer adjusts the speed of the siderostat by means of the controls on the electronic device in right foreground.
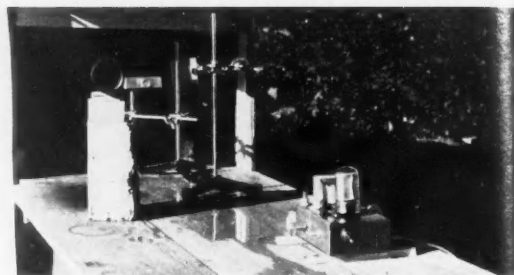

wavelength bands, more efficient detectors than the present types of photographic plates are needed. Increased sensitivity could also be obtained from balloon-, rocket-, and artificial satellite-based spectrographs. Excellent results have already been obtained in this way on the spectrum of the Sun, revealing hitherto undetected portions in the infrared as well as in the ultraviolet.

TABLE 1. *Absorption bands of* H_2O *in the red and infrared portions of the spectrum*

The second column gives, for each band, the associated quantum numbers for the three fundamental modes of vibration (stretching, bending, and distortion) of the H_2O molecule. The relative transition probabilities are a measure of the intrinsic intensity of the absorption lines.

Wavelength of band head	Vibrations ν_1,ν_2,ν_3	Relative transition probability
μ		
1.379	1, 0, 1	>6
1.135	1, 1, 1	1.000
0.942	2, 0, 1	0.3
.823	2, 1, 1	.1
.723	3, 0, 1	.03
.652	3, 1, 1	.005

[1] *For further technical details, see* High-dispersion spectra of Mars, *by C. C. Kiess, C. H. Corliss, Harriet K. Kiess, and Edith L. R. Corliss, Astrophys. J.* **126,** *579 (November 1957).*

[2] *Mauna Loa observatory for high-altitude research, NBS Tech. News Bul.* **40,** *137 (October 1956).*

[3] *The B band of oxygen in the spectrum of Mars, by W. S. Adams and T. Dunham, Jr., Astrophys. J.* **79,** *308 (1934); Some results with the coudé spectrograph of the Mount Wilson Observatory, by W. S. Adams and T. Dunham, Jr., Astrophys. J.* **93,** *16 (1941).*

[4] *Private communication from E. K. Plyler and W. S. Benedict (1956).*

[5] *Wavelengths of rotational lines in the water-vapor bands at 0.93 and 1.13 microns, by C. C. Kiess, J. Research NBS* **48,** *377 (1952) RP2325.*

Impact Test for Leather

IN CONNECTION with basic studies on the properties of materials, a machine has been developed to evaluate the strength, stretch, and "crackiness" of leathers. Designed by T. J. Carter of the leather laboratory, the device delivers repeated thrusts to both sides of a specimen until failure. From the data on grain cracking and elongation obtained during the breaking-down process, the physical properties of the material can be determined. The machine is expected to be of value in developing better leathers for shoe uppers.[1]

Investigations of the physical properties of leather, especially those properties important to the development of better leathers for footwear, have been intensified in recent years. But techniques used to evaluate these properties have not been fully effective because of the lack of homogeneity in leathers. The strength of leather has usually been measured in only one direction, either parallel or perpendicular to the backbone of the hide. As most leather is used for shoes, a method has been needed to measure its strength, stretch, and tendency to crack, independent of direction. The present equipment provides such a method; thus it affords

a valuable tool for comparing various tannages and leather lubricants, and is useful as a means of detecting deterioration caused by various kinds of exposure.

Two hemispherical-tipped plungers attached to reciprocal shafts are supported horizontally in the same axial plane on a 2- by 4-ft stand. The leather specimen is held in an upright position between the plungers by serrated steel plates provided with central apertures $1\frac{1}{2}$ in. in diameter. Identical cams driven in opposite directions of rotation by an electric motor alternately activate the plungers. Force is applied to the specimen by 27-pound weights attached through openings in the stand to the two plunger assemblies. During a test, the plungers break down the leather specimen by striking the two sides alternately at the rate of 44 impacts a minute.

The diameter of the plungers used in the current investigation ranged from 0.250 to 0.875 in. Results indicate that the number of impacts before failure increases with an increase in plunger diameter. It was observed that the amount of stretch on impacting is inversely proportional to the diameter of the plunger.
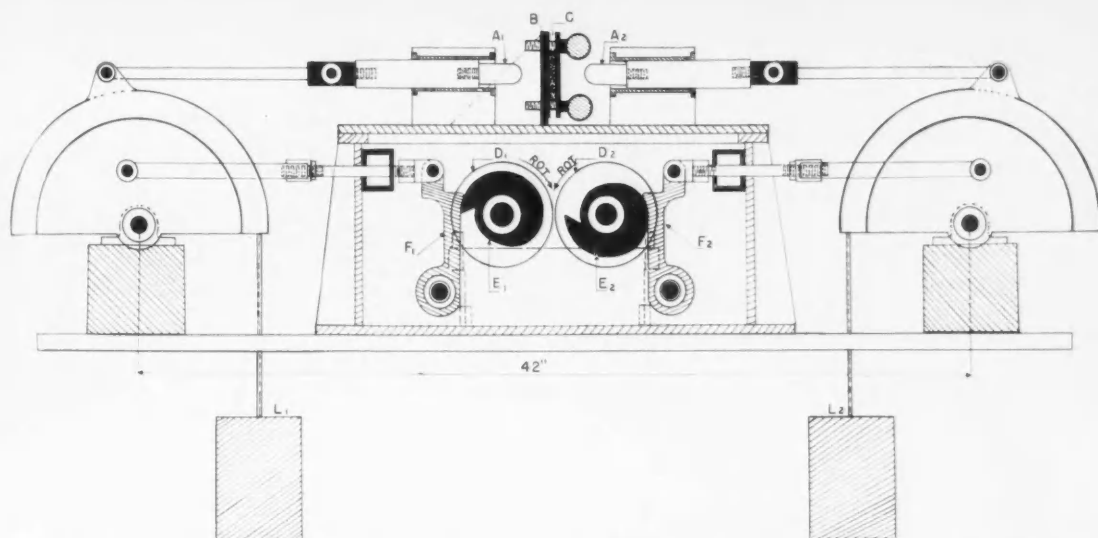
Cross section of machine used to test leather. A_1 and A_2—plungers; B—clamp assembly; C—leather specimen; D_1 and D_2—gears; E_1 and E_2—cams; F_1 and F_2—cam followers; L_1 and L_2—weights.

Equipment for testing leather's strength, stretch, and tendency to crack. Specimen is being removed from assembly that clamps the specimen between two plungers. One plunger may be noted to the right of the specimen.

and that the number of impacts required to produce grain cracking is directly proportional to the diameter.

The effect of leather thickness on resistance to breakdown was investigated. It was found that the logarithm of the number of impacts before failure, plotted against the logarithm of weight per unit thickness, gives an approximately straight-line relation.

A comparative study of the durability, as judged by the impact tester, of typical upper leather showed that the resistance to breakdown is greatest for straight chrome-tanned leather containing stuffing mixture, and lowest for chrome-vegetable tanned leather containing grease. Straight chrome-tanned leather containing fat-liquor is less resistant to impact breakdown than chrome-tanned leather containing stuffing mixture.

Investigations were made of the impact resistance of variously tanned, greased, and degreased leathers aged for 96 hr at temperatures of 80°, 100°, and 120° C. The fat-liquored, straight chrome-tan and all the degreased leathers showed marked deterioration between 100° and 120° C. regardless of the type of tannage.

Tanned and lubricated leathers were exposed both to outdoor and to simulated tropical aging before testing in the impact machine. Chrome-syntan leather and fat-liquored straight chrome-tanned leather were found to be the least susceptible to deterioration under outdoor exposure. However, after tropical exposure, these types showed the highest percentage loss in resistance to impacting.

In determining the effects of different amounts of lubricant on impact resistance, it was found that each increment of lubricant improved the strength of the leather up to a maximum point. After that, either there was no further improvement in strength or an actual decrease occurred as additional amounts of lubricant were applied. The stretch and tendency to crack of the grain were not appreciably affected by increases in the amount of the lubricants.

[1] *For further technical details, see* An impact test for leather based on an alternating punching force, *by* Thomas J. Carter, J. Am. Leather Chemists' Assoc. (in press).

Preserving

Documents

by Lamination

THE USE OF LAMINATING FILM to preserve and repair old or damaged documents has been investigated as part of a continuing program of research on the preservation of records. After comparing the stability of many films, specifications for a laminating film suitable for archival use have been established. The investigation was sponsored by the National Archives, the Library of Congress, the Army Map Service, and the Virginia State Library.

Laminating equipment used by document restorers includes a flatbed steam-heated hydraulic press and a roller-type press with electrically preheated platens. In the process, a "sandwich" is made by placing the paper between sheets of cellulose acetate, which are then bonded to the paper with heat and pressure. The current study was undertaken with the following objec-

Paper-tensile tester. A torn specimen is being removed from the special-edge tear device. With this device, the stress concentration is directed to the edge of the specimen by a metal angle behind which one end of the specimen is clamped.

tives: (1) To develop information necessary to compile specifications for cellulose acetate of commercially practicable quality with the maximum stability for lamination; (2) to determine whether pretreatment of documents with alkaline media is necessary or desirable before lamination; (3) to determine the increased tear and folding endurance resulting from the use of tissue reinforcement; (4) to investigate the effect of lamination on paper; and (5) to make a preliminary study of the newer plastic films to determine their acceptability for laminating documents.

The investigation began with a study of the degradation of two cellulose acetate films, a commercial film and a laboratory film, over a wide temperature range and under a variety of conditions. The results showed that oxidation was the most important environmental factor in the degradation of these films.

Although the effect of water vapor was not studied extensively, somewhat more degradation occurred in moist oxygen than in dry oxygen. Pyrolytic degradation was negligible in comparison with oxidative degradation.

On the basis of the data obtained with these two films, a temperature of 124° C and an atmosphere of flowing oxygen (saturated with water vapor at 30° C) were selected for the study of a large number of commercial films and laboratory formulations. The stability of commercial films was found to vary over a wide range. Although lack of stability is of little importance in many of the commercial uses for which these films are produced, only a film with high-stability characteristics can be used to restore documents that must last for centuries.

The softening point of unplasticized cellulose acetate is too high to permit lamination. Thus a plasticizer is necessary to reduce the softening point sufficiently to permit lamination at a temperature low enough to prevent degradation. A study of several laboratory formulations showed that the type of plasticizer and the presence of acid and salts in the film are significant factors in degradation. Films containing ester plasticizers with an aliphatic ether linkage were highly susceptible to oxidation. Triphenyl phosphate appeared to impart considerable stability to film formulations.

The physical properties of a laminating film are set within fairly narrow limits by the plasticizer requirements. To determine the change in physical properties with degradation, stress-strain data were obtained on some specimens in various stages of deterioration. The elongation decreased as degradation increased until the

yield point was reached, after which tensile strength decreased sharply with degradation. Loss of plasticizer did not appear to be a problem, as the stress-strain curves and folding endurance values did not change appreciably with plasticizer loss. The last traces of an active solvent plasticizer were held more tenaciously than a less-active plasticizer. Films 0.001-in. thick cast without plasticizer were quite flexible even though their elongation was less than that of a plasticized film.

Other investigators had demonstrated that even a small amount of sulfuric acid in a film formulation is deleterious. However, sulfuric acid has been customarily used as a catalyst in the acetylation reaction in the manufacture of cellulose acetate. Most of the "bound sulfate" is removed during purification but it is not practicable to remove the last traces. Bound sulfate is normally neutralized by traces of calcium or magnesium salts in the acetate. If a film formulation contains an acid acceptor, such as magnesium acetate or calcium acetate, degradation due to bound sulfate or free acid is minimized. When a combination of acid acceptors, antioxidants, and the proper plasticizer was used, a film of superior stability, measured by the rate of degradation in moist oxygen at 124° C, was obtained.

Some document restorers neutralize the acid in the paper before lamination. To evaluate this process, a rag paper and a wood pulp paper with varying amounts of added acid were deacidified and these, together with specimens that had not been deacidified, were subjected to accelerated aging. Deacidification prevented most of the damage by acid during accelerated aging, when tensile strength, degree of polymerization, and reflectance were used as the criteria of degradation. Some damage was suffered by film laminated to acid paper, but this was small compared to the degradation of the paper.

The heat and pressure customarily used in lamination were found to have no measurable effect on the film. The effect on the paper also was negligible in the ab-

Removing film from glass plate after solvent has evaporated.

sence of acid, but if the paper contained an appreciable quantity of acid, the degradation during lamination was found to be very serious, especially if the press was held at a high-operating temperature. Thus, the process of deacidification is beneficial if a document contains enough acid to cause appreciable degradation during lamination. A comparison of typical laminating presses in the Washington, D. C., area indicated that, if proper attention is given to the operating variables, time, temperature, and pressure, satisfactory laminates can be made on either the flatbed or the cylindrical presses.

The use of tissue paper to reinforce the structure was found to enhance most of the measurable physical properties of a laminated paper. Tensile strength, internal tearing strength, and bursting strength of the laminate were increased. However, the edge-tear resistance of a laminate prepared with film and tissue was slightly less than that of a laminate prepared only with film.

A preliminary study was made of several plastic films other than cellulose acetate. The results indicated that cellulose propionate, cellulose acetate-propionate, polyethylene, and polyethylene terephthalate films merited further study for use as archival films. It would be necessary, however, to investigate the stability of these films. Also, a suitable adhesive for bonding polyethylene terephthalate to paper and a means for removing polyethylene and polyethylene terephthalate films from documents would be needed.

Wide range of stability of cellulose acetate films as measured by rate of degradation in oxygen at 124° C. Intrinsic fluidity, the reciprocal of intrinsic viscosity, was used as the criterion of degradation.

TECHNICAL
NEWS
BULLETIN

Contents

Publications of National Bureau of Standards

Periodicals

Journal of Research of the National Bureau of Standards, Volume **60**, No. 2, February 1958 (RP2824 to RP2832 incl.). 60 cents. Annual subscription $4.00, $1.25 additional for foreign mailing.
Technical News Bulletin, Volume **42**, No. 2, February 1958. 10 cents. Annual subscription $1.00, 35 cents additional for foreign mailing.
Basic Radio Propagation Predictions for May 1958. Three months in advance. CRPL-D 162. Issued February 1958. 10 cents. Annual subscription $1.00, 25 cents additional for foreign mailing.

Research Papers

Journal of Research, Volume 60, No. 2, February 1958. 60 cents.
RP2824. Energy spectra of cascade electrons and photons. Charles A. Olson and Lewis V. Spencer.
RP2825. Observer differences in color-mixture functions studied by means of a pair of metameric grays. Kenneth L. Kelly.
RP2826. Precise evaluation of surface area with indirectly calculated dead space. William V. Loebenstein.
RP2827. Sample calculations of gamma-ray penetration into shelters: Contributions of sky shine and roof contamination. Martin J. Berger and James C. Lamkin.
RP2828. Heat content of sodium borohydride and of potassium borohydride from 0°C to 400°C. Thomas B. Douglas and Ann W. Harman.
RP2829. Infrared spectra of crystalline polyphenyls. James E. Stewart and Max Hellmann.
RP2830. On the application of steam-driven water jets for propulsion purposes. J. M. Burgers and A. Ghaffari.
RP2831. Mass spectra and relative sensitivities of some polyphenyls. Paul Bradt and Fred L. Mohler.
RP2832. Infrared spectra of thermally degraded poly(vinyl chloride). Robert R. Stromberg, Sidney Straus, and Bernard G. Achhammer.

Applied Mathematics Series

AMS49. Further contributions to the solution of simultaneous linear equations and the determination of eigenvalues. 50 cents.

Miscellaneous Publications

M222. Report of the 42d National Conference on Weights and Measures 1957. 55 cents.

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High-repetition-rate mercury pulser. L. Costrell. Nucleonics. **15**, No. 11, 112 (1957).
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Publications for which a price is indicated are available only from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. (foreign postage, one-fourth additional.) The three NBS periodicals are available on a 1-, 2-, or 3-year subscription basis, although no reduction in rates can be made. Reprints from outside journals and the NBS Journal of Research may often be obtained directly from the authors.

Patents

(The following United States Patents have been granted to NBS inventors. Assigned to United States of America, as represented by the Secretary of the Department noted in parentheses.)

No. 2,809,004. October 8, 1957. Holders for electronic components. Joseph Kaufman and Clarence P. Skenes (Army).
No. 2,817,073. December 17, 1957. Multichannel tape system of storage. John R. Sorrells (Commerce).
No. 2,817,759. December 24, 1957. Crystal-stabilized pulse-pair generator. Moody C. Thompson, Jr. (Commerce).
No. 2,817,787. December 24, 1957. Cathode-ray-tube sweeps. Leslie S. G. Kovasznay. (Licensed to the United States Government as represented by the Secretary of Commerce.)

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